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14. ABSTRACT
Schrödinger's equation for atoms and molecules supports solutions that are not totally antisymmetric under electron coordinate permutations. These non-Pauli eigenstates are generally regarded as unphysical, with interest in them centered largely on their role as possible ``contaminants" in physical solutions constructed by methods that provide only approximate antisymmetry, such as exchange perturbation theories, many-body diagrammatic approaches, and variational methods in the absence of precise prior enforcement of basis-state antisymmetry. Here we report atomic and molecular non-Pauli Schröodinger solutions employing largely pedestrian methods as an alternative to the more complicated Wigner-Weyl approach based on theory of the symmetric group. Using the non-relativistic Hamiltonian operator and spin-orbital product representations in variational calculations, we show that every antisymmetric Schröodinger eigenstate of an n electron atom or molecule is accompanied by 2^n-1 degenerate non-Pauli ``ghost" solutions. As a consequence of this degeneracy, admixtures of non-Pauli states are always present in Pauli solutions having only approximate antisymmetry. These can significantly affect calculated expectation values, even in the face of precise energy predictions.

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On the Non-Pauli States of Atoms and Molecules[a]

J.D. Mills & P.W. Langhoff, AFRL/UCSD

- The Schrödinger equation allows "non-Pauli" solutions.
- A formal theory was given by Wigner and Weyl.
- A pedestrian variational approach is described here.
- Non-Pauli states can "contaminate" antisymmetric states.[b]

a - Supported by AFOSR/AFRL/NRC

b - Theor. Chem. Accts. **120**, 199-213 (2008).

The Central Ideas

- An unrestricted Hartree product of atomic spin orbitals is complete for Pauli and non-Pauli Schrödinger eigenstates.

- The non-relativisitic Hamiltonian matrix in this representation can be constructed employing standard methods.

- Pauli and non-Pauli states can be separated *ex post facto*.[a]

- Totally antisymmetric Schrödinger eigenstates are always accompanied by 2^n-1 degenerate non-Pauli ghost states.

a - Chem. Phys. Lett. **358**, 231-236 (2002)

The Basic Equations

Schrödinger equation:

$$\hat{H}(\boldsymbol{r})\boldsymbol{\Psi}(\boldsymbol{r}) = \boldsymbol{\Psi}(\boldsymbol{r}) \cdot \mathbf{E}$$

Non-relativistic Hamiltonian operator:

$$\hat{H}(\boldsymbol{r}) = \sum_{i=1}^{n} \Big\{ -\frac{\hbar^2}{2m}\nabla_i^2 - \frac{Ze^2}{r_i} + \sum_{j=i+1}^{n} \frac{e^2}{r_{ij}} \Big\}$$

Spin-orbital Hartree-product representation:

$$\boldsymbol{\Phi}(\boldsymbol{r}) = \{\boldsymbol{\phi}(\boldsymbol{1}) \otimes \boldsymbol{\phi}(\boldsymbol{2}) \otimes \cdots \boldsymbol{\phi}(\boldsymbol{n})\}_O$$

Spin-orbital row vector:

$$\boldsymbol{\phi}(\boldsymbol{i}) = \{1s\alpha(\boldsymbol{i}), 1s\beta(\boldsymbol{i}), 2s\alpha(\boldsymbol{i}), 2s\beta(\boldsymbol{i}), ...\}$$

A Simple Example - Atomic Helium

Two spin orbitals:

$$\boldsymbol{\phi}(1) = \{1s\alpha(1), 1s\beta(1)\}, \qquad \boldsymbol{\phi}(2) = \{1s\alpha(2), 1s\beta(2)\}$$

Spin-orbital Hartree-product representation:

$$\boldsymbol{\Phi}(1,2) = \{\boldsymbol{\phi}(1) \otimes \boldsymbol{\phi}(2)\}_O$$

$$= 1s(1)1s(2)\,\{\alpha(1)\alpha(2), \alpha(1)\beta(2), \beta(1)\alpha(2), \beta(1)\beta(2)\}$$

Hamiltonian operator:

$$\hat{H}(\boldsymbol{r}) = \sum_{i=1}^{2} \Big\{ -\frac{\hbar^2}{2m}\nabla_i^2 - \frac{2e^2}{r_i} \Big\} + \frac{e^2}{r_{12}}$$

Atomic Helium - Energy Matrix

Hamiltonian matrix:

$$\mathbf{H} \equiv \langle \mathbf{\Phi}(\boldsymbol{r}) | \hat{H}(\boldsymbol{r}) | \mathbf{\Phi}(\boldsymbol{r}) \rangle$$

$$= \begin{pmatrix} E_{1s^2} & 0 & 0 & 0 \\ 0 & E_{1s^2} & 0 & 0 \\ 0 & 0 & E_{1s^2} & 0 \\ 0 & 0 & 0 & E_{1s^2} \end{pmatrix}$$

$$E_{1s^2} = 2\langle 1s(1)| - \frac{\hbar^2}{2m}\nabla_{\mathbf{1}}^2 - \frac{2e^2}{r_1}|1s(1)\rangle$$
$$+\langle 1s(1)1s(2)|\frac{e^2}{r_{12}}|1s(1)1s(2)\rangle$$

Atomic Helium - Spin Eigenstates

Spin singlet eigenstate (S=0):

$$1s(1)1s(2)\frac{1}{\sqrt{2}}\left\{\alpha(1)\beta(2) - \beta(1)\alpha(2)\right\}(M_S = 0)$$

Spin triplet eigenstates (S=1):

$$1s(1)1s(2)\left\{\alpha(1)\alpha(2)\right\}(M_S = +1)$$

$$1s(1)1s(2)\frac{1}{\sqrt{2}}\left\{\alpha(1)\beta(2) + \beta(1)\alpha(2)\right\}(M_S = 0)$$

$$1s(1)1s(2)\left\{\beta(1)\beta(2)\right\}(M_S = -1)$$

Another Example - Atomic Lithium

Four spin orbitals for each electron:

$$\boldsymbol{\phi}(1) = \{1s\alpha(1), 1s\beta(1), 2s\alpha(1), 2s\beta(1)\}$$

$$\boldsymbol{\phi}(2) = \{1s\alpha(2), 1s\beta(2), 2s\alpha(2), 2s\beta(2)\}$$

$$\boldsymbol{\phi}(3) = \{1s\alpha(3), 1s\beta(3), 2s\alpha(3), 2s\beta(3)\}$$

Spin-orbital Hartree-product representation (64 terms):

$$\boldsymbol{\Phi}(1,2,3) = \{\boldsymbol{\phi}(1) \otimes \boldsymbol{\phi}(2) \otimes \boldsymbol{\phi}(3)\}_O$$

Atomic Lithium - Basis Functions

Spin (8) and space (8) basis functions:

$$\boldsymbol{\Phi}(\boldsymbol{r}) = \boldsymbol{\Phi}_{space}(\boldsymbol{r}) \otimes \boldsymbol{\Phi}_{spin}(\boldsymbol{r})$$

$$\begin{aligned}\boldsymbol{\Phi}_{spin}(\boldsymbol{r}) = \{&\alpha(1)\alpha(2)\alpha(3), \alpha(1)\alpha(2)\beta(3), \alpha(1)\beta(2)\alpha(3),\\ &\alpha(1)\beta(2)\beta(3), \beta(1)\alpha(2)\alpha(3), \beta(1)\alpha(2)\beta(3),\\ &\beta(1)\beta(2)\alpha(3), \beta(1)\beta(2)\beta(3)\}\end{aligned}$$

$$\begin{aligned}\boldsymbol{\Phi}_{space}(\boldsymbol{r}) = \{&1s(1)1s(2)1s(3), 1s(1)1s(2)2s(3), 1s(1)2s(2)1s(3),\\ &1s(1)2s(2)2s(3), 2s(1)1s(2)1s(3), 2s(1)1s(2)2s(3),\\ &2s(1)2s(2)1s(3), 2s(1)2s(2)2s(3)\}\end{aligned}$$

Atomic Lithium - Energy Matrix

Hamiltonian matrix:

$$\mathbf{H} \equiv \langle \mathbf{\Phi}(\boldsymbol{r}) | \hat{H}(\boldsymbol{r}) | \mathbf{\Phi}(\boldsymbol{r}) \rangle$$

$$\mathbf{\Phi}(\boldsymbol{r}) = \mathbf{\Phi}_{space}(\boldsymbol{r}) \otimes \mathbf{\Phi}_{spin}(\boldsymbol{r})$$

$$\mathbf{H} = \begin{pmatrix} \mathbf{H}_{8x8} & \mathbf{0} & \cdot & \cdot & \mathbf{0} \\ \mathbf{0} & \mathbf{H}_{8x8} & \cdot & \cdot & \mathbf{0} \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \mathbf{0} & \mathbf{0} & \cdot & \cdot & \mathbf{H}_{8x8} \end{pmatrix}_{64x64}$$

$$\mathbf{H}_{8x8} \equiv \langle \mathbf{\Phi}_{space}(\boldsymbol{r}) | \hat{H}(\boldsymbol{r}) | \mathbf{\Phi}_{space}(\boldsymbol{r}) \rangle$$

Atomic Lithium - Energy (au) Ladder

Pauli States (theory/exp.)		**Non-Pauli States**
	-	-1.766 (8)
	-	-5.202 (8)
$(1s2s^2)^2$S(+1/2)	-5.232/-5.323	-5.232 (7)
$(1s2s^2)^2$S(-1/2)	-5.232/-5.323	-5.232 (7)
	-	-7.348 (8)
$(1s^22s)^2$S(+1/2)	-7.433/-7.476	-7.433 (7)
$(1s^22s)^2$S(-1/2)	-7.433/-7.476	-7.433 (7)
	-	-8.422 (8)

Atomic Lithium - In Summary

- There are 8 unique energies each of which is 8-fold degenerate
- There are 4 Pauli states $(1s^2 2s)^2 S(\pm 1/2)$, $(1s 2s^2)^2 S(\pm 1/2)$
- There are 20 totally symmetric states
- There are 40 mixed symmetry states
- Each physical state has 7 degenerate non-Pauli states

Generalizations

- The Hartree product always factors; $\mathbf{\Phi}(\boldsymbol{r}) = \mathbf{\Phi}_{space}(\boldsymbol{r}) \otimes \mathbf{\Phi}_{spin}(\boldsymbol{r})$.
- The dimension of $\mathbf{\Phi}_{spin}(\boldsymbol{r})$ is 2^n for n electrons.
- The dimension of $\mathbf{\Phi}_{space}(\boldsymbol{r})$ is arbitrarily large.
- Every physical Schrödinger state has $2^n - 1$ non-Pauli ghosts.
- The number of non-Pauli states increases rapidly with n.
- Degenerate non-Pauli states can contribute to physical states in the absence of precise total antisymmetry.
- Such mixed states can provide accurate energies but can include significant non-Pauli contributions to physical expectation values.